# VAPOR PRESSURES OF SATURATED AQUEOUS SALT SOLUTIONS OF SELECTED INORGANIC SALTS

by

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ABSTRACT

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The vapor pressure of saturated aqueous salt solutions as functions of temperature have been measured for lithium bromide, lithium iodide, sodium bromide, potassium hydroxide, cesium fluoride, and zinc bromide. The temperature range is about plus 5°C. to 70°C., with this range extended from minus 10°C. to plus 105°C. for lithium bromide and restricted to plus 5°C. to 35°C. for sodium bromide. Vapor pressures, water activities, and heats of vaporization and solution are tabulated at 5°C. intervals except in the vicinities of changes of hydration of the solid phase, where pressures and activities are plotted with sufficient frequency to show details. The experimental uncertainty in pressure is $\pm$ 10 x $10^{-3}$ millibars and that in the heat of solution is $\pm$ 2 percent.

## FOREWORD

The apparatus and measurements described in this paper are a continuation of work previously described [1]. The original work consisted in constructing the apparatus, developing the experimental procedure, and performing measurements on seventeen salts, primarily those for which reliable published data existed at at least one temperature. Of the seventeen, only twelve could be compared (at 25 degrees Celsius) with published data of comparable accuracy [2]. Agreement within experimental error was obtained in ten of twelve comparison cases, indicating the apparatus and techniques employed were capable of yielding accurate vapor pressure measurements. The two salts for which substantial disagreement existed were reexamined as part of the study conducted as the thesis project. The data previously obtained by the author were confirmed for magnesium chloride, but the remeasurement of sodium bromide provided a small correction which brought the data into agreement with that published.

In addition to the remeasurement, the present study was intended to measure the vapor pressures of saturated solutions possessing very low water activities as a function of temperature and to investigate the thermodynamic treatment of the data obtained.

Solutions with low water activity are useful in humidity measurement. A saturated solution comes into equilibrium with atmospheric water vapor when the vapor pressure of that solution equals the partial pressure of water vapor in the atmosphere. So long as the vapor pressure of the solution is a single-valued function of temperature, this temperature

is a unique measure of atmospheric humidity. Although low water activity solutions are not required in principle, in practice they lend great simplicity to the design and operation of a hygrometer.

The thermodynamic treatment of saturated salt solutions in this thesis is limited only to that applicable to the data obtained; namely the vapor pressure and the derivative of vapor pressure with respect to temperature. Solubility data from other sources have not been employed in numerical calculations.

## ACKNOWLEDGMENTS

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# INTRODUCTION

A knowledge of the water vapor pressures of saturated solutions of inorganic salts is useful in the control and measurement of humidity and as the complement to other thermodynamic data on saturated and unsaturated solutions. Data are presented over a fairly broad temperature range for lithium bromide, lithium iodide, sodium bromide, potassium hydroxide, cesium fluoride , and zinc bromide. Particular attention has been devoted to the accurate determination of the vapor pressures in the regions of hydrate transitions in the solid phase. The temperature range of the measurements was subject to the limitations of the apparatus, and will be discussed in this context below, but is generally from plus 5 degrees Celsius to plus 70 degrees Celsius. Although the precision of the data ($\pm$ 10 x $10^{-3}$ millibars) is not immediately useful in the control and measurement of humidity, since the effect of air or other gas remains unaccounted for in the technique employed, the accuracy is thermodynamically useful since it is reasonably consistent with the accuracy of data available for unsaturated solutions. Briefly, this technique consisted of measuring the vapor pressures of saturated solutions with a very accurate U-tube mercury manometer. The apparatus is described in some detail below, but its most significant attribute is that accurate measurements may be made quickly with a high degree of confidence.

## APPARATUS

The apparatus employed in these measurements is shown in Figures 1, 2, and schematically in Figure 3. It may be considered in three categories: the manometer, the sample system, and the temperature control and measurement system.

The manometer is essentially a large bore U-tube, the connection passage being drilled through the stainless steel base. A crossover valve provides connection and isolation of the two spaces over the mercury column as well as access for the vacuum pump to the sample system. Column height is measured with micrometers reading directly in ten-thousandths of an inch. Provision for leveling and its indication are made with three screws and two sensitive bubbles. Two "O" rings accomplish sealing of each micrometer and the crossover valve stem. These three pairs of "O" rings are arranged in the top block in such a manner that a long drilled hole intercepts the space between any pair. This hole exits over the right hand column, so a vacuum is continuously drawn between any pair of "O" rings, effectively eliminating any leakage into the pressurized column or sample system. This device, in conjunction with adequate sealing elsewhere, resulted in a leak-free system.

The sample system, as may be seen from Figure 3, consists of two stopcocks, $S_1$ for convenient isolation from the manometer and $S_2$ to permit initial evacuation with a mechanical pump, a taper joint $J_1$ for raising and lowering of the salt in and out of the bath, a 50 milliliter Ehrlenmeyer flask to contain the solution, and a magnetic stirrer. Continuous agitation was believed to be very desirable, although this was

not firmly established. A Fisher Isotemp water bath furnished an adjustable temperature constant to within $\pm$ 0.005°C. A Meyers platinum resistance thermometer and an L&N G-1 thermometer bridge accurately measured the bath temperature. Shortly before use in these measurements, the bridge was calibrated by NBS and these values used to establish the resistance of the thermometer at the triple point of water. Since this resistance differed by only $10 \times 10^{-4}$ ohms from a previous calibration of the thermometer, this small amount was added to all resistance values of the previous calibration and the bath temperature determined accordingly. One additional precaution was taken; a small air-conditioned box was constructed and used to maintain the bridge temperature about the same value at which NBS performed the calibration.

Without special modification to the apparatus, the temperature range was limited to +5°C at the lower end since the water bath would not function adequately below this temperature. Again, without modification, the temperature was limited at the higher end to 70 or 75°C by the water bath; but in any case, the measured vapor pressure could not exceed that of the saturated vapor pressure of pure water at room temperature (25°C) since condensation would occur on the walls of the sample system or manometer. This latter restriction applied only to sodium bromide in the present study, but did set the upper temperature limit in the previous work for sixteen of seventeen salts.

Special modifications necessary to extend the temperature range were made to perform measurements on lithium bromide since this salt is of great interest in humidity measurement. To extend the lower end of the range, an antifreeze solution replaced the water in the bath and the refrigerator extracting heat from the bath was permitted to run over-

night to lower the temperature to -10°C. To extend the upper end of the range, the water in the bath was replaced by paraffin oil; while the portion of the sample system exposed to the room air was wrapped in heating wire and a 600 watt electric heater was placed in front of the fan circulating air over the manometer.

## EXPERIMENTAL PROCEDURE

After about five grams of a salt was totally dissolved in distilled water and the 50 milliliter flask sealed to the sample system, the solution was degassed by cooling to $0^{\circ}C$ and evacuating through stopcock $S_2$, warmed to $25^{\circ}C$, and sufficient water vaporized to saturate the solution by evacuating with the diffusion pump through stopcock $S_1$ and the manometer. A measurement was performed at $25^{\circ}C$, followed by a further, brief evacuation with the diffusion pump, and then a second measurement at $25^{\circ}C$. The two measurements were required to agree within $\pm$ 10 x $10^{-3}$ mb before subsequent data at other temperatures were obtained.

By increasing or decreasing the bath temperature in $5^{\circ}C$ intervals without removing the water vapor pressure from the manometer unless the solution required resaturation, the data could be accumulated quite easily. The attainment of equilibrium was determined by allowing the bath temperature to stabilize for ten minutes, then taking two or more readings at ten minute intervals until two consecutive readings agreed to within $\pm$ 1 x $10^{-4}$ inches on each micrometer. More than two readings were infrequently required. After the lowest (or highest) temperature for a given day was attained, the bath was returned to the initial temperature of that day and this measurement repeated. Agreement well within the experimental error was obtained for every salt for which data are presented below.

In the original work during which intermediate evacuation to reestablish saturation was not usually necessary, one further check was made. By maintaining pressure on the manometer and cooling the solution to the dry ice point, water vapor condensed and its pressure made entirely

negligible. Any residual pressure remaining must be accounted for by either a leak or insufficient degassing of the solution prior to the measurements. Since leakage was ruled out by the fact that repetition of a measurement on two days without degassing on the second yielded the same value for the vapor pressure, the residual pressure (never exceeding $10 \times 10^{-3}$ mb) could easily be subtracted from the experimental values with confidence.

However, in the present work the solubility of the salts varied so rapidly that the removal of water from the solution to maintain saturation was commonly necessary between temperature steps. These intermediate evacuations obviated any attempt to measure residual pressure. Accordingly, a different procedure was instituted. In a manner similar to that of the initial degassing and saturation, at least two readings at saturation, separated by a brief evacuation, were taken and required to agree with $\pm 10 \times 10^{-3}$ mb. This repeatability check is two-fold: saturation and a thorough degassing are assured. This frequent testing for saturation assumed paramount importance during the measurements on lithium iodide. This salt is photosensitive, so the entire sample system up to the taper joint was made light tight, obviating any visual determination of saturation.

One further point deserves mention. The laboratory, and metropolitan Washington, D. C., are plagued by ground vibrations which created small standing waves in the mercury surface. The effect of these was minimized by allowing the pointed micrometer tip to first depress the mercury surface, then slowly raising the micrometer until this small depression just disappeared. This technique, with proper lighting of the mercury surface, proved most satisfactory.

## UNCERTAINTY AND SYSTEMATIC ERRORS IN THE MEASUREMENTS

### 1. Uncertainty

In assigning an uncertainty to the data, possible errors from several sources must be considered. The general formula for obtaining the vapor pressure from the manometer and temperature measurements is:

$$e(T_b) = gC \frac{(h_{\ell o}-h_{\ell}) + (h_r-h_{ro})}{1+\beta T_{Hg}} = gC \frac{(h_{\ell o}-h_{ro})+h_r-h_{\ell}}{1+\beta T_{Hg}} \qquad (1)$$

$$C = 33.864 \frac{\text{millibars}}{\text{inch Hg at } 0^{\circ}C} \qquad g = \frac{980.090}{980.665} = 0.999414$$

$$\beta = 1.818 \times 10^{-4}/^{\circ}C$$

$e(T_b)$ = vapor pressure at the bath temperature $T_b$

$h_{\ell o}$ = left micrometer reading with equal pressure on both columns

$h_{ro}$ = right micrometer reading with equal pressure on both columns

$h_{\ell}$ = left micrometer reading with vapor pressure on left column

$h_r$ = right micrometer reading with vapor pressure on left column

In the original work, both micrometers were checked against gauge blocks over a three-quarter inch range and found accurate within $\pm 2 \times 10^{-5}$ inches. This error may be neglected. With vacuum over both columns of mercury, the quantity $h_{\ell o}-h_{ro}$ in equation (1) was determined. By repeating this measurement 100 times and plotting the difference from the mean obtained on each measurement vs. its frequency, a curve approximating a normal distribution was obtained and a value of $\pm 7 \times 10^{-5}$ inches assigned for the mean standard deviation. This value is independent of the mercury temperature, but dependent upon the consistency with which the manometer

could be leveled. In the original work, the average value of this distribution was found to be $h_{\ell o}-h_{ro} = 0.99967$, but after 12 months of disuse between the original and the present measurements, this value was found to have shifted to 0.99940, probably because of the evaporation of about 0.006 inches of mercury from each column in conjunction with the slightly nonuniform bores of the two legs. This value, $h_{\ell o}-h_{ro}=0.99940$ was applied to calculating all the present measurements and the uncertainty originally obtained, $\pm 0.00007$ inches, which includes that of leveling, was taken over from the original work. Subsequent "zero difference" measurements taken at the beginning and end of each day confirmed the average value chosen. Taking the total differential of equation (1)

$$\Delta e(T_b) = Cg \frac{\Delta(h_{\ell o}-h_{ro}) + \Delta h_r - \Delta h_\ell}{1 + \beta T_{Hg}} - Cg \frac{[(h_{\ell o}-h_{ro}) + h_r - h_\ell]\beta \Delta T_{Hg}}{(1+\beta T_{Hg})^2}$$

$$\Delta e(T_b) \approx [\Delta(h_{\ell o}-h_{ro}) + \Delta h_r - \Delta h_\ell] - e(T_b)\beta \Delta T_{Hg} \qquad (2)$$

$$\text{if} \quad \beta T_{Hg} \ll 1 \quad \text{and} \quad g \approx 1$$

By assigning the value $\pm 7 \times 10^{-5}$ inches to $h_r$ and $h_\ell$ as well as to $(h_{\ell o}-h_{ro})$ and $\pm 0.5^{\circ}C$ to $T_{Hg}$, and pessimistically choosing the errors to be additive, equation (2) becomes:

$$\Delta e(T_b) \approx \pm 34(21 \times 10^{-5}) \pm (9 \times 10^{-5})\, e(T_b) \qquad (3)$$

Since $e(T_b)$ did not exceed 34 mbs:

$$\Delta e(T_b) \leq \pm 10 \times 10^{-3} \text{ mb.}$$

Thus, an uncertainty of $\pm 10 \times 10^{-3}$ mbs is assigned to any vapor pressure value shown in Tables III to VIII, except as noted in the following paragraph.

In the measurement of the vapor pressure of a saturated solution of lithium bromide above $75^{\circ}C$, the manometer was heated to about $42^{\circ}C$ by

heating the air circulated over the manometer. As might be expected, the heating was not uniform so a much larger value than $\pm 0.5^{\circ}C$ must be applied to $\Delta T_{Hg}$ .

By estimating $\Delta T_{Hg} = \pm 2.5^{\circ}C$ and noting that $e(T_b)$ assumes a maximum value of about 64 millibars, equation (3) may be rewritten as

$$\Delta' e(T_b) \approx \pm 34(21 \times 10^{-5}) \pm (45 \times 10^{-5})\ 64 \qquad (3')$$

$$\Delta' e(T_b) \approx \pm\ 35 \times 10^{-3}\ \text{mb}. \qquad (4')$$

Internal consistency of the experimental data was checked by computing the water activity for each temperature shown in Tables III to VIII and plotting these values. All points for each salt between hydrate transition temperatures lie within experimental accuracy on smooth, regular curves.

## 2. Systematic Errors

The question of equilibrium is central to the measurement of vapor pressure. Several tests confirmed that equilibrium was indeed attained in these measurements.

In the original work, the rate of reaching equilibrium was specifically tested by allowing the bath temperature and vapor pressure to reach equilibrium, then changing the bath temperature and recording vapor pressure and bath temperature vs. time. Figure 4 shows the result for magnesium chloride.

A test for saturation was conducted on each salt. An excess of the solid phase was visually confirmed and the solution allowed to reach equilibrium with its vapor for about ten minutes, then readings were taken at ten-minute intervals until two agreed (again, most often only

two were required). Opening the crossover valve removed some water from the solution, requiring the reestablishment of equilibrium. If the equilibrium returned to the same vapor pressure, it returned within 20 minutes. If it did not return within 20 minutes, it never did reach the same pressure value, even after waiting several hours. A third confirmation of the rapid attainment of equilibrium can be inferred from the vapor pressure values obtained when approaching the same bath temperature from a lower and then a higher temperature. By using the same procedure of allowing ten minutes for equilibrium followed by two readings at ten-minute intervals, values for vapor pressure within the experimental uncertainty were obtained for both cases.

Other sources of systematic error might arise from irregular capillary depression of the mercury, an incorrect density of mercury, pressure over the right or vacuum column, off-vertical positioning of the micrometers, impurity of the salts, and leakage and residual gas. Leakage and residual gas have been treated above and shown not to be sources of systematic error.

Capillary depression is entirely negligible. The bore of both manometer legs is 51 millimeters, which corresponds to a capillary depression less than $2 \times 10^{-4}$ millimeters of mercury [3].

Since triple distilled virgin mercury is used, any deviations from the standard density of 13.5951 grams per cubic centimeter, estimated at $\pm 4 \times 10^{-6}$ parts by Stimson [4] is also negligible.

As shown in Figure 1, the pressure over the right mercury column was monitored by a McLeod gauge. It regularly indicated a pressure of 1 micron or less, a negligible quantity.

As noted above, the two micrometers were checked against gauge blocks and showed an accuracy of at least $\pm$ 2 x $10^{-5}$ inches over a three-quarter inch range. This check was made in the following manner. Both micrometers were mounted in the finished top block prior to assembly of the manometer. The block was then elevated above a level, smooth steel plate and the blockadjusted to level along both horizontal axes. Sufficient gauge blocks were added or removed beneath the micrometer tips to allow checking a three-quarter inch range. The micrometers were accurate to $\pm$0.00002 inches when the brass block was level. After assembly of the complete manometer, the level of the top block could easily be transferred to the two bubble levels mounted on the stainless steel base. Since the three bubble levels used were of comparable sensitivity (4 x $10^{-4}$ radians), a simple calculation shows that negligible error arose because of any deviation from the vertical of the micrometers.

The effect of impurities in the salts was evaluated for one case during the original work. A salt mixture of approximately 1% by weight zinc chloride and 99% sodium chloride was prepared and measurements of its vapor pressure made. The results are shown in Table I with those for reagent grade sodium chloride.

Most salts studied were reagent grade or optical quality crystals. Only zinc bromide was not included among these, being available only as "Purified". The only salt possessing a listed impurity in excess of 0.1% was potassium hydroxide, which was contaminated with 0.4% potassium carbonate.

TABLE I

VAPOR PRESSURES OF NaCl AND NaCl PLUS 1% $ZnCl_2$

| Salt | Temperature °C | Vapor Pressure mb |
|---|---|---|
| NaCl + $ZnCl_2$ | 15 | 12.876 |
| NaCl | 15 | 12.884 |
| NaCl + $ZnCl_2$ | 20 | 17.613 |
| NaCl | 20 | 17.640 |

As another check of accuracy, the vapor pressure of pure water was measured at about 20°C.

TABLE II

| Temperature °C | Experimental Vapor Pressure | Smithsonian Tables (1951) [5] mb |
|---|---|---|
| 20.018 | 23.401 | 23.399 |
| 20.016 | 23.395 | 23.396 |

One source of systematic error may not have been negligible during the measurements of the vapor pressure of lithium iodide. As noted above, it is photosensitive, decomposing to yield iodine which does not have a negligible vapor pressure at the temperatures employed. The salt was exposed only to a darkroom light during filling of the 50 milliliter flask, and dissolved in distilled water slowly while being maintained at the ice point. As a visual check, a portion of glass tubing adjacent to stopcock $S_1$ was cooled with dry ice which would condense both water and

iodine vapor. No discoloration of the ice condensed could be seen. Although the possibility of iodine contributing to the measured pressure cannot be excluded, the assumption is made that it did not.

## THERMODYNAMIC TREATMENT OF THE DATA

From the plots of vapor pressure vs. temperature of saturated salt solutions only two thermodynamically significant quantities are available: the pressure itself and the derivative of pressure with respect to temperature. However, several other important quantities may be derived from these two.

To an excellent approximation [6]:

$$a_w = p/p^o \tag{5}$$

$a_w$ = water activity of the solution at temperature T

$p$ = vapor pressure of the solution at temperature T

$p^o$ = vapor pressure of pure water at temperature T

By the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H_v}{T(v''' - \Delta v^c)} \tag{6}$$

T = absolute temperature

$\Delta H_v$ = quantity of heat which must be supplied to the system to vaporize one mole of water at temperature T

$v'''$ = molal volume of water vapor at temperature T [1]

$\Delta v^c$ = change in volume of the condensed phases of the system at temperature T when one mole of water is vaporized.

By definition:

$$RT \ln a_w = \mu_w - \mu_w^o \tag{7}$$

R = gas constant

$\mu_w$ = chemical potential of water in the solution at temperature T

1. Since the system under consideration is univariant, specification of T automatically specifies p .

$\mu_w^o$ = chemical potential of pure water at temperautre T

One may also differentiate equation (7) with respect to T to obtain:

$$\frac{d\ln a_w}{dT} = \frac{\bar{H}_w - H_w^o}{RT^2} \tag{8}$$

$\bar{H}_w$ = partial molal enthalpy of water in the solution at temperature T

$H_w^o$ = molal enthalpy of water at temperature T

To an excellent approximation [7,8]:

$$\frac{d\ln a_w}{dT} = -\frac{\Delta H_s}{RT^2} = \frac{Q_s}{RT^2} \tag{9}$$

$\Delta H_s$ = change in enthalpy when one mole of liquid water goes into solution with sufficient solid phase to form a saturated solution at temperature T

$Q_s$ = heat of solution taken positive for heat liberated

Before obtaining any other quantities of thermodynamic interest, the system must be considered in some detail. The system in question consists of three phases; $n_w'''$ moles of pure water vapor, $n_w''$ moles of water plus $n_s''$ moles of anhydrous salt in solution, and $n_w'$ moles of water plus $n_s'$ moles of anhydrous salt in the solid or crystalline phase. The following must be true:

$$\begin{aligned} n_w'/n_s' &= \alpha \\ n_w''/n_s'' &= r \\ n_w' + n_w'' + n_w''' &= n_w = \text{constant} \\ n_s' + n_s'' &= n_s = \text{constant} \end{aligned} \tag{10}$$

$\alpha$, the number of water molecules of hydration is constant in a tem-

perature interval between hydrate phase transitions. r is, in general, a function of temperature. Equations (10) may be slightly modified by taking $\Delta n_w'''$ as being the number of moles of water which enter the vapor phase in any given process (i.e., vaporization of $\Delta n_w'''$ moles of water); and so forth for the other four quantities to yield for a process at any given temperature:

$$\begin{aligned} \Delta n_w'/\Delta n_s' &= \alpha \\ \Delta n_w''/\Delta n_s'' &= r \\ \Delta n_w' + \Delta n_w'' + \Delta n_w''' &= 0 \\ \Delta n_s' + \Delta n_s'' &= 0 \end{aligned} \tag{11}$$

Equations (11) may be combined to yield the following:

$$\begin{aligned} \Delta n_w' &= -\alpha/\alpha-r\ \Delta n_w''' \\ \Delta n_w'' &= r/\alpha-r\ \Delta n_w''' \\ \Delta n_s' &= -1/\alpha-r\ \Delta n_w''' \\ \Delta n_s'' &= 1/\alpha-r\ \Delta n_w''' \end{aligned} \tag{12}$$

Equations (12) lead to an interesting result. Consider the process wherein one mole of pure liquid water at temperature T is added to exactly the right amount of the crystalline phase to form a saturated solution:

$$1 + \Delta n_w'/\Delta n_s' = r \tag{13}$$

Since $\Delta n_w' = \alpha \Delta n_s'$

$$\Delta n_s' = 1/r-\alpha \tag{14}$$

Consider the results of adding one mole of pure liquid water to the correct amounts of the crystalline phases that can coexist at the temperature of a hydrate transition, $T_t$. Assume that at $T_t$ the higher hydrate loses one molecule of hydration.

$$H_2O[\ell] + [1/r-\alpha]S \cdot \alpha H_2O[c] = [1/r-\alpha]S\cdot rH_2O[s]\ \Delta H = -\Delta H_s^{\alpha}$$

$$H_2O[\ell] + [1/r-(\alpha-1)]S\cdot(\alpha-1)H_2O[c] = [1/r-(\alpha-1)]S\cdot rH_2O[s]\Delta H = -\Delta H_s^{\alpha-1} \quad (15)$$

Multiplying the first of equations (15) by $r-\alpha$ and the second by $r-\alpha+1$:

$$(r-\alpha)H_2O[\ell]+S\cdot\alpha H_2O[c] = S\cdot rH_2O[s]\ \Delta H = -(r-\alpha)\Delta H_s^{\alpha}$$

$$(r-\alpha+1)H_2O[\ell]+S\cdot(\alpha-1)H_2O[c] = S\cdot rH_2O[s]\ \Delta H = -(r-\alpha+1)\Delta H_s^{\alpha-1} \quad (16)$$

Subtracting the second of equations (16) from the first:

$$S\cdot\alpha H_2O[c] = S\cdot(\alpha-1)H_2O[c]+H_2O[\ell]\ \Delta H = (r-\alpha+1)\Delta H_s^{\alpha-1}-(r-\alpha)H_s^{\alpha} \quad (17)$$

But equation (17) is just the hydrate transition at temperature $T_t$, where $H = \Delta H_h$, the heat which must be supplied to remove one mole of water from one mole of the higher hydrate.

$$\Delta H_h = (r-\alpha+1)\ \Delta H_s^{\alpha-1} - (r-\alpha)\ \Delta H_s^{\alpha} \quad (18)$$

From equation (9)

$$\Delta H_h = (r-\alpha)RT_t^2\left[\frac{d\ln aw}{dT}\right]_{T_t,\alpha} - (r-\alpha+1)RT_t^2\left[\frac{d\ln aw}{dT}\right]_{T_t,\alpha-1} \quad (19)$$

Summing up, the vapor pressure vs. temperature data for saturated aqueous salt solutions provides the necessary experimental data to compute at a variety of temperatures the water activity of the solution, the latent heat of vaporization, the integral heat of solution, and with a knowledge of the solubility of the salt and the chemical potential of pure water, the heat of hydration at the transition temperatures and chemical potential of water in the solution. Furthermore, other tabulated data on unsaturated solutions would permit the calculation of any other desired thermodynamic quantity of saturated solutions, such as the activity coefficients of water and salt, partial molal entropies, and so forth.

## DATA

The data are presented in Tables III to VIII. Since the experimental values of vapor pressure were not obtained at exactly even intervals of five degrees Celsius, a normalization calculation was made. This consisted of linear interpolation to obtain the value of the vapor pressure gradient of pure water at the experimental temperature and calculation of the vapor pressure of pure water at the experimental temperature. This value could then be employed to calculate the water activity of the saturated solution by equation (5). With the assumption that the activity is constant over a small temperature interval, multiplication of the activity by the previously calculated vapor pressure gradient of pure water yielded a similar figure for the saturated solution. The vapor pressure of the saturated solution could then easily be normalized to the desired $5^{o}C$ interval. In no case did the normalizations involve temperature differences in excess of $60 \times 10^{-3o}C$. In the regions of phase transitions, the experimental vapor pressures were plotted vs. temperature on an expanded scale and a best-fitting, smooth curve drawn. From this curve, vapor pressures at convenient temperature intervals and that of the transition temperature were extracted.

Although numerous plots have been devised and described in the literature [9] to yield straight lines for vapor pressure data, the presence of the solid phase in the system under consideration renders these techniques virtually useless. Since scaling is much more convenient on linear than full logarithmic or semi-logarithmic paper, the vapor pressures computed for convenient temperature intervals were substituted into equation

(5) and activities at the same temperatures computed. The variation of activity with temperature is very much smaller than that of vapor pressure; furthermore, activities frequently lend themselves to plotting a derived function, $a_w'$, on a very expanded linear scale. This derived function is related to the activity by:

$$a_w'(T) = a_w(T) - [A+B(T-T_o)] \tag{20}$$

A and B are constants and $T_o$ some reference temperature, all being arbitrarily chosen for convenience in plotting $a_w'(T)$ vs. T for a given salt. In particular:

$$da_w'/dT = da_w/dT - B \tag{21}$$

By plotting either $a_w$ or $a_w'$ vs. temperature on an expanded scale which readily displayed the experimental error, a smooth, best-fitting curve could be drawn within the uncertainty for each value of $a_w$ or $a_w'$. From these curves, smoothed values of $a_w$ and $da_w/dT$ were obtained. These values of $a_w$ appear in Tables III-VIII and were used to compute the vapor pressures that are given there. The values of $da_w/dT$ were employed to compute the values of $\Delta H_v$ and $Q_s$ that are given.

The vapor pressures were calculated directly by rewriting equation (5):

$$p = a_w p^o \tag{22}$$

The heats of solution were computed from equation (9):

$$Q_s = RT^2 \frac{d\ln a_w}{dT} \tag{23}$$

The heats of vaporization were calculated by taking logrithms of both sides of equation (22), differentiating with respect to T, and multiplying by $RT^2$. These steps result in the following equation

$$RT^2 \frac{d\ln p}{dT} = RT^2 \frac{d\ln a_w}{dT} + RT^2 \frac{d\ln p^o}{dT} \qquad (24)$$

By assuming water vapor to behave as a perfect gas, neglecting $\Delta v^c$ in comparison with $v'''$ in equation (6), and doing the same with the Clapeyron equation for vapor in equilibrium with pure water, equation (24) may be rewritten to yield:

$$\Delta H_v = Q_s + L_w \qquad (25)$$

$L_w$ is the latent heat of vaporization of pure water and is tabulated in references [5] and [10]. A satisfactory, but most laborious, means of determining the accuracy of $da_w/dT$ is to also graphically measure $dp/dT$, compute the differential logarithms of both quantities, and substitute into equation (24) and compare with the tabulated values of $L_w$. Enough comparisons of this sort will supply a reasonable estimate of the uncertainty, but not systematic error, in $da_w/dT$. A simpler procedure was followed. In the region of a phase transition, expanded linear plots of vapor pressure vs. temperature may be made. The vapor pressures of two salts [2], lithium chloride and potassium hydroxide, pass through maxima there. The temperature at which $dp/dT = 0$, $T_m$, may be reasonably estimated and equation (24) rewritten:

$$RT_m^2 \left[\frac{1}{a_w} \frac{da_w}{dT}\right]_{T_m} = -RT_m^2 \left[\frac{1}{p^o} \frac{dp^o}{dT}\right]_{T_m} \qquad (26)$$

These two comparisons indicate an uncertainty of at least $\pm 0.7\%$, and more conservatively $\pm 2\%$, should be applied to the measured values of $da_w/dT$ and correspondingly to the values $Q_s$ given in Tables III to VIII.

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2. Cesium fluoride should be included, but insufficient data were taken in the region of the phase transition to make an accurate plot.

TABLE III

LITHIUM BROMIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| -10 | 0.0903 | 0.259 | 42.13 | - 3.35 |
| - 5 | 0.0876 | 0.369 | 41.54 | - 3.73 |
| 0 | 0.0848 | 0.518 | 40.82 | - 4.23 |
| 5 | 0.0818 | 0.713 | 39.93 | - 4.90 |
| 10 | 0.0786 | 0.965 | 39.09 | - 5.53 |
| 15 | 0.0752 | 1.282 | 37.92 | - 6.49 |
| 20 | 0.0714 | 1.669 | 36.49 | - 7.70 |
| 25 | 0.0673 | 2.131 | 34.52 | - 9.46 |
| 30 | 0.0627 | 2.660 | 32.0 | -11.8 |
| 35 | 0.0577 | 3.244 | 28.3 | -15.3 |
| 36 | 0.0564 | 3.352 | | |
| 37 | 0.0551 | 3.461 | | |
| 38 | 0.0539 | 3.569 | | |
| 39 | 0.0526 | 3.677 | | |
| 40 | 0.0513 | 3.785 | 22.7 | -20.6 |
| 41 | 0.0500 | 3.890 | | |
| $41.96T_t$ [3] | 0.0488 | 3.991 | 21.2 | -22.1 |
| $41.96T_t$ | 0.0488 | 3.991 | 46.82 | 3.56 |
| 42 | 0.0488 | 3.999 | | |
| 43 | 0.0490 | 4.232 | | |
| 44 | 0.0491 | 4.470 | | |
| 45 | 0.04926 | 4.722 | 45.89 | 2.76 |
| 50 | 0.05003 | 6.174 | 45.51 | 2.60 |
| 55 | 0.05075 | 7.991 | 45.11 | 2.43 |
| 60 | 0.05137 | 10.236 | 44.60 | 2.13 |
| 65 | 0.05190 | 12.983 | 44.06 | 1.80 |
| 70 | 0.05237 | 16.323 | 43.71 | 1.67 |
| 75 | 0.05280 | 20.358 | 43.25 | 1.42 |
| 80 | 0.05313 | 25.17 | 42.66 | 1.05 |
| 85 | 0.05331 | 30.82 | 41.81 | 0.42 |
| 90 | 0.05336 | 37.41 | 41.03 | - 0.13 |
| 95 | 0.05327 | 45.03 | 40.26 | - 0.67 |
| 100 | 0.05304 | 53.74 | 39.43 | - 1.26 |
| 105 | 0.05266 | 63.61 | 38.31 | - 2.13 |

3. $T_t$ denotes the transition temperature of the solid phase.

TABLE IV

LITHIUM IODIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| 5 | 0.2155 | 1.879 | 39.10 | - 5.73 |
| 10 | 0.2058 | 2.526 | 38.30 | - 6.32 |
| 15 | 0.1961 | 3.342 | 37.42 | - 6.99 |
| 20 | 0.1862 | 4.352 | 36.53 | - 7.66 |
| 25 | 0.1762 | 5.580 | 35.48 | - 8.50 |
| 30 | 0.1660 | 7.043 | 34.35 | - 9.42 |
| 35 | 0.1557 | 8.756 | 33.1 | -10.5 |
| 40 | 0.1452 | 10.712 | 31.4 | -11.9 |
| 45 | 0.13450 | 12.892 | 29.5 | -13.6 |
| 50 | 0.12352 | 15.242 | 27.2 | -15.7 |
| 55 | 0.11215 | 17.659 | 24.2 | -18.5 |
| 60 | 0.10016 | 19.958 | 19.8 | -22.7 |
| 65 | 0.08708 | 21.784 | 13.2 | -29.1 |
| 66 | 0.08439 | 22.073 | | |
| 67 | 0.08149 | 22.279 | | |
| 68 | 0.07847 | 22.419 | | |
| 69 | 0.07532 | 22.479 | | |
| 70 | 0.07201 | 22.445 | | |
| 71 | 0.06843 | 22.268 | | |
| 72 | 0.06455 | 21.924 | | |
| 73 | 0.06010 | 21.300 | | |
| 74 | 0.05475 | 20.242 | -70 | -112 |

TABLE V

SODIUM BROMIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| 5 | 0.6374 | 5.558 | 41.94 | - 2.89 |
| 10 | 0.6229 | 7.644 | 41.48 | - 3.14 |
| 15 | 0.6080 | 10.363 | 40.98 | - 3.43 |
| 20 | 0.5929 | 13.858 | 40.51 | - 3.68 |
| 25 | 0.5776 | 18.293 | 40.00 | - 3.98 |
| 30 | 0.5619 | 23.841 | 39.50 | - 4.27 |
| 35 | 0.5460 | 30.705 | 39.00 | - 4.56 |

TABLE VI

POTASSIUM HYDROXIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| 5 | 0.1310 | 1.142 | 36.58 | - 8.25 |
| 10 | 0.1222 | 1.500 | 34.3 | -10.3 |
| 15 | 0.1121 | 1.911 | 31.3 | -13.1 |
| 20 | 0.1008 | 2.356 | 27.3 | -16.9 |
| 25 | 0.0883 | 2.797 | 21.8 | -22.2 |
| 30 | 0.0739 | 3.136 | 11.6 | -32.2 |
| 31 | 0.0707 | 3.176 | | |
| 32 | 0.0673 | 3.200 | | |
| 32.5 | 0.0656 | 3.209 | | |
| 33 | 0.0637 | 3.205 | | |
| 33.5 | 0.0618 | 3.200 | | |
| 33.86$T_t$ | 0.0606 | 3.195 | - 7.5 | -51.1 |
| 33.86$T_t$ | 0.0606 | 3.195 | 46.05 | 2.43 |
| 34 | 0.0606 | 3.223 | | |
| 35 | 0.0606 | 3.408 | 42.85 | - 0.71 |
| 40 | 0.0600 | 4.425 | 41.12 | - 2.22 |
| 45 | 0.05909 | 5.664 | 40.37 | - 2.76 |
| 50 | 0.05805 | 7.163 | 39.60 | - 3.31 |
| 55 | 0.05691 | 8.961 | 38.91 | - 3.77 |
| 60 | 0.05568 | 11.095 | 38.12 | - 4.35 |
| 65 | 0.05432 | 13.589 | 37.24 | - 5.02 |
| 70 | 0.05275 | 16.442 | 35.38 | - 6.66 |

TABLE VII

CESIUM FLUORIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| 5 SC [4] | 0.0174 | 0.152 | 52.36 | 7.53 |
| 10 SC | 0.0183 | 0.225 | 50.77 | 6.15 |
| 15 SC | 0.0191 | 0.325 | 49.60 | 5.19 |
| 20 SC | 0.0197 | 0.461 | 48.71 | 4.52 |
| 25 SC | 0.0203 | 0.644 | 48.12 | 4.14 |
| 30 SC | 0.0209 | 0.886 | 47.58 | 3.81 |
| 35 SC | 0.0214 | 1.202 | 46.87 | 3.31 |
| 40 | 0.0218 | 1.609 | 46.10 | 2.76 |
| 45 | 0.02215 | 2.123 | 45.47 | 2.34 |
| 50 | 0.02243 | 2.768 | 44.92 | 2.01 |
| 55 | 0.02265 | 3.556 | 44.27 | 1.59 |
| 60 | 0.02283 | 4.549 | 43.77 | 1.30 |
| 65 | 0.02297 | 5.746 | 43.22 | 0.96 |
| 70 | 0.02308 | 7.194 | 42.92 | 0.88 |
| 75 | 0.02317 | 8.933 | 42.54 | 0.71 |
| 5 | 0.0676 | 0.589 | 36.46 | - 8.37 |
| 10 | 0.0629 | 0.772 | 34.2 | -10.4 |
| 15 | 0.0578 | 0.985 | 31.6 | -12.8 |
| 20 | 0.0521 | 1.218 | 27.7 | -16.5 |
| 25 | 0.0456 | 1.444 | 21.0 | -23.0 |
| 30 | 0.0379 | 1.608 | 8.3 | -35.5 |
| 35 | 0.0273 | 1.535 | -27.6 | -71.2 |

4. SC denotes supercooled values.

TABLE VIII

ZINC BROMIDE

| Temperature °C | Activity | Vapor Pressure millibars | $\Delta H_v$ $10^3$ joules/mole | $Q_s$ $10^3$ joules/mole |
|---|---|---|---|---|
| 5 | 0.0870 | 0.759 | 43.53 | - 1.30 |
| 10 | 0.0860 | 1.055 | 42.90 | - 1.72 |
| 15 | 0.0848 | 1.445 | 42.15 | - 2.26 |
| 20 | 0.0830 | 1.940 | 40.34 | - 3.85 |
| 25 | 0.0801 | 2.536 | 37.62 | - 6.36 |
| 30 | 0.0762 | 3.234 | 33.98 | - 9.79 |
| 31 | 0.0751 | 3.373 | | |
| 32 | 0.0739 | 3.514 | | |
| 33 | 0.0726 | 3.650 | | |
| $33.91T_t$ | 0.0710 | 3.758 | 27.7 | -15.9 |
| $33.91T_t$ | 0.0710 | 3.758 | 48.81 | 5.19 |
| 34 | 0.0710 | 3.777 | | |
| 35 | 0.0715 | 4.019 | 48.71 | 5.15 |
| 40 | 0.0736 | 5.426 | 48.28 | 4.94 |
| 45 | 0.07596 | 7.281 | 48.03 | 4.90 |
| 50 | 0.07811 | 9.639 | 47.60 | 4.69 |
| 55 | 0.08020 | 12.628 | 47.33 | 4.65 |
| 60 | 0.08225 | 16.389 | 46.99 | 4.52 |
| 65 | 0.08421 | 21.066 | 46.66 | 4.40 |
| 70 | 0.08611 | 26.840 | 46.23 | 4.19 |

## SUMMARY

The apparatus and techniques described in this paper lend themselves to the rapid and accurate measurement of the water vapor pressures of saturated salt solutions as a function of temperature with an uncertainty of $\pm$ 10 x $10^{-3}$ millibars. For this thesis project measurements have been made on six salts and these supplement previous measurements on seventeen salts. The temperature range for which data was obtained is about plus $5^{\circ}C$ to $70^{\circ}C$, but extended to minus $10^{\circ}C$ and plus $105^{\circ}C$ in one case. The data is internally consistent and compares well with published data of comparable accuracy.

For the sake of accuracy, consistency, and convenience, the experimental values of vapor pressures were plotted as activities vs. temperature on expanded scales and a smooth curve drawn within the bounds of experimental error at each point. From these curves smoothed values of activity were read off, tabulated, and used to compute the tabulated vapor pressures. By drawing tangents to these same curves at desired temperatures, the temperature derivatives of activity were obtained and used to compute heats of solution and vaporization. The accuracy of this graphical procedure for determining derivatives is conservatively estimated at $\pm$ 2 percent.

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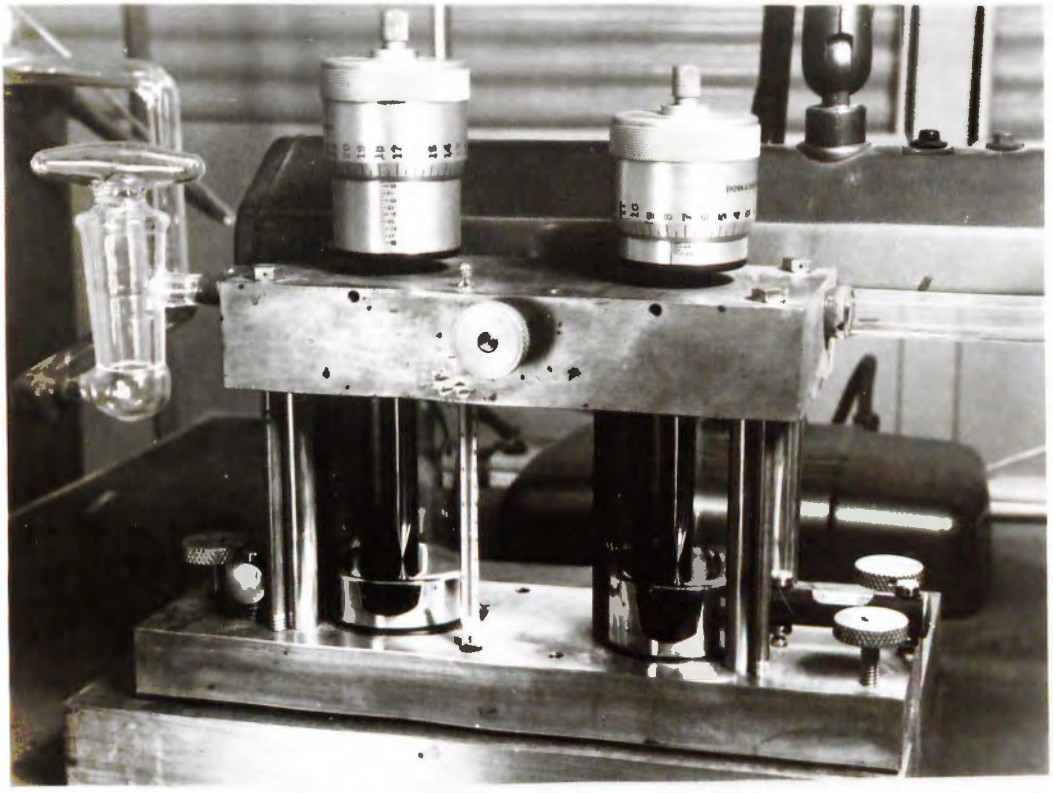


FIGURE 1 MANOMETER

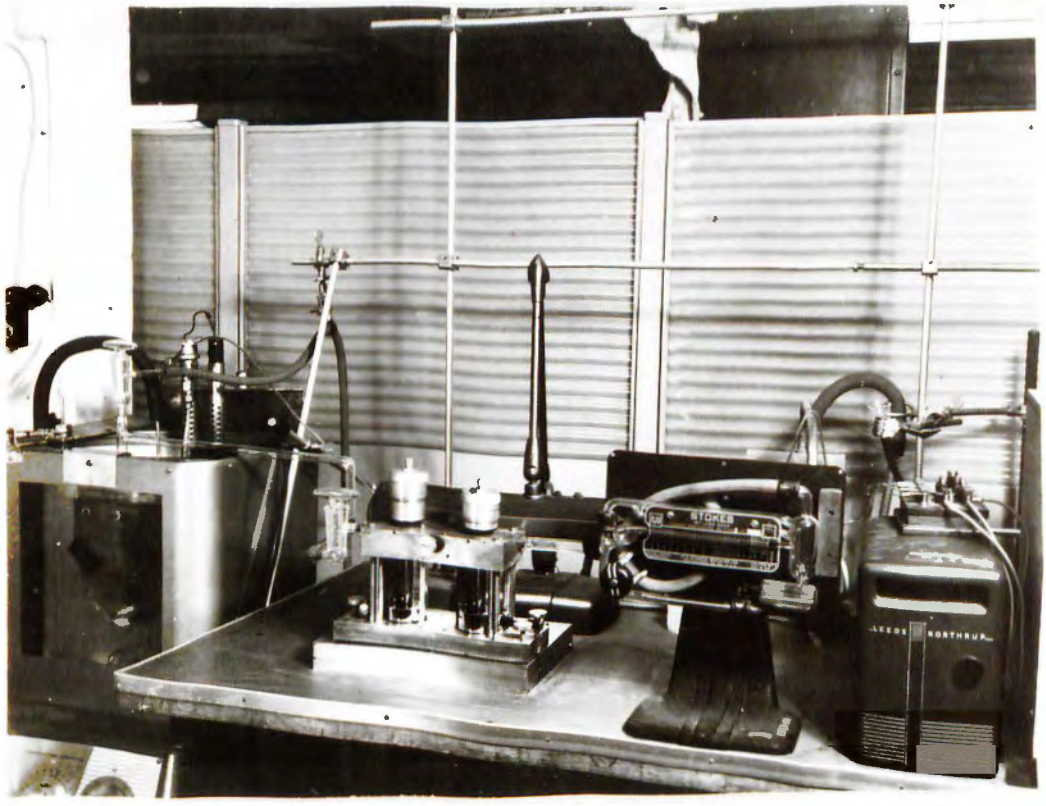
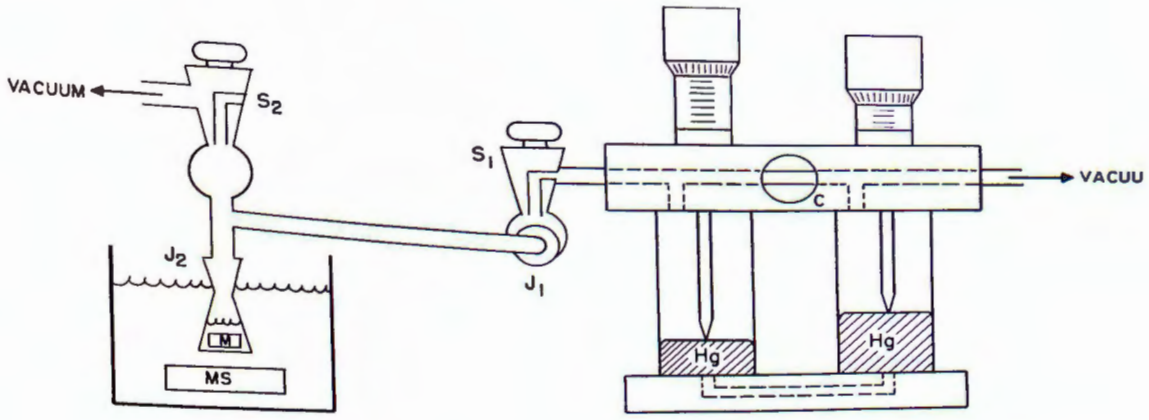


FIGURE 2 APPARATUS




$S_1$ & $S_2$ - STOPCOCKS

$J_1$ - TAPERED GLASS JOINT - PERMITING REMOVAL OF SOLUTION FROM BATH

$J_2$ - TAPERED GLASS JOINT - SEALING FLASK TO SAMPLE SYSTEM

MS - MAGNETIC STIRRER

M - MAGNET

C - CROSSOVER VALVE

FIGURE 3 APPARATUS SCHEMATIC

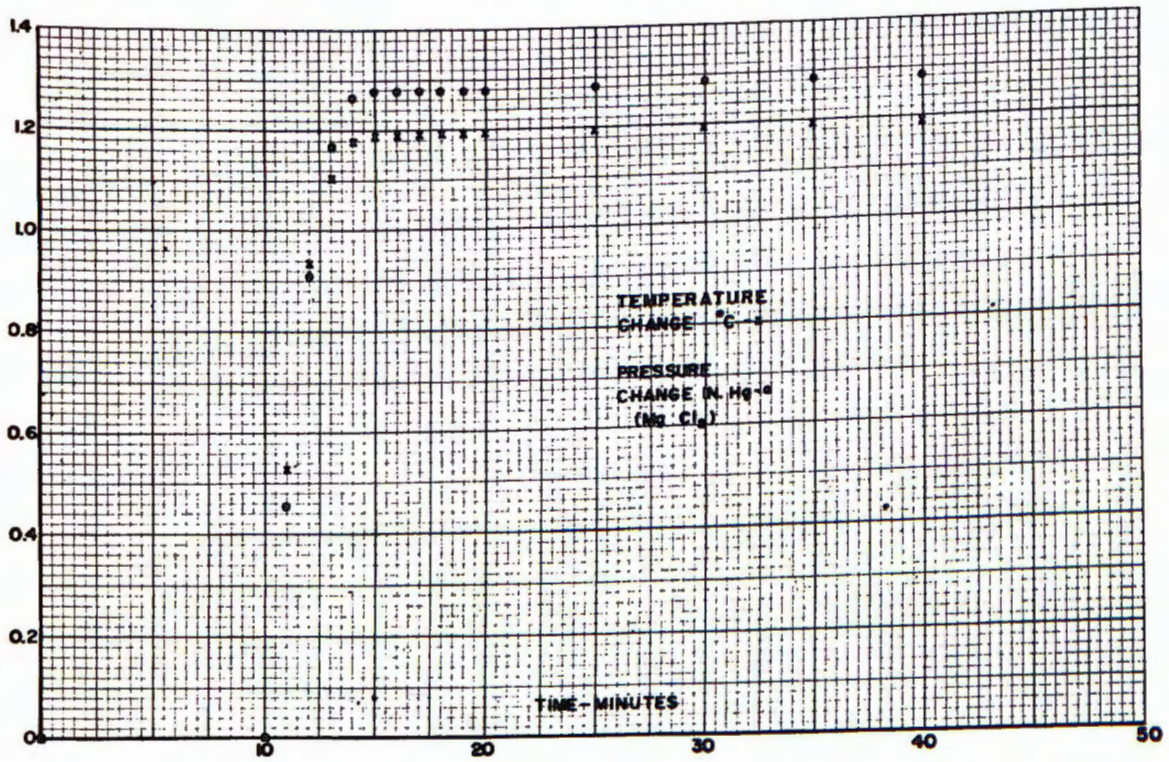



FIGURE 4 TEMPERATURE AND PRESSURE CHANGE vs TIME FOR $MgCl_2$